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X-ray Molecular Structures of $[Co_3(CO)_9C](\mu_3\text{-}CS_2)[Co_3(CO)_7S]$ and $[Co_3(CO)_8](\mu_5\text{-}CS_2)[Co_3(CO)_7S]$: Two Different Ways of Bonding of CS_2 to Tricobalt Units and a New Type of a Semiclosed Semicarbidic Heavy-Atom Cluster

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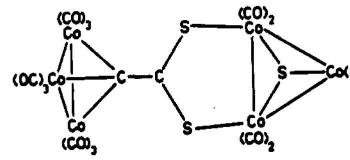
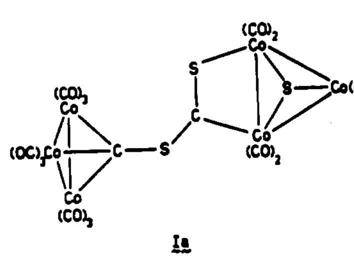
Two related compounds obtained in the reaction of $Co_2(CO)_8$ with CS_2 at room temperature have been fully characterized by X-ray diffraction analysis: $Co_6(CO)_{16}C_2S_3$ (V) is triclinic, $P\bar{1}$, with $a = 12.822$ (4) Å, $b = 13.399$ (4) Å, $c = 8.851$ (4) Å, $\alpha = 100.07$ (4)°, $\beta = 85.72$ (3)°, $\gamma = 106.20$ (4)°, $Z = 2$, and $\lambda(\text{Mo K}\alpha) = 0.7107$ Å; $Co_6(CO)_{15}CS_3$ (Ib) is triclinic, $P\bar{1}$, with $a = 14.131$ (4) Å, $b = 10.580$ (4) Å, $c = 9.768$ (4) Å, $\alpha = 95.58$ (3)°, $\beta = 83.83$ (3)°, $\gamma = 111.33$ (4)°, $Z = 2$, and $\lambda(\text{Mo K}\alpha) = 0.7107$ Å. The cobalt atoms were localized by the conventional Patterson method and the C, O and S atoms by subsequent difference-Fourier maps. The final R values are 0.066 (V, 3224 reflections) and 0.023 (Ib, 3730 reflections) for intensities with $I > 3\sigma(I)$ in both cases. Both molecules contain two Co_3 subclusters that are connected by different types of CS_2 bridges. In each case one of the Co_3 units is $Co(CO)_7S$. For V the other subcluster is a regular $(CO)_9Co_3C$ pyramid, whereas in Ib an unprecedented $(CO)_8Co_3CS_2$ entity has been found in which the CS_2 fragment is, through the C atom as well as through both sulfur atoms, thoroughly bonded to an isosceles Co_3 triangle containing an extremely short (2.440 (1) Å) Co–Co bond. IR spectra are analyzed both in the region of the vibrations of the CS_2 unit and in the C–O stretching region. In complex V bands at 1167, 991, and 742 cm^{-1} are assigned to $C_{ap}\text{–}C(S_2)$ and to the asymmetric and symmetric C–S stretching vibrations, respectively, of the bridging CS_2 unit. Ib has been obtained also from $^{13}CS_2$, and the spectrum of the ^{13}C-enriched species has also been studied. The bands at 870 and 729 cm^{-1} undergo an isotopic shift of 28 and 25 cm^{-1}, respectively, and are hence related to the vibrations of the C atom of the Co_3CS_2 subcluster. An interpretation is offered that would explain the experimental fact that only about half of the IR-active C–O stretching modes can be observed.

Introduction

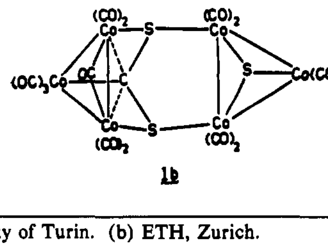
Recently we published preliminary results about the preparation and structure of a new cobalt carbonyl–carbon disulfide derivative in which a $Co_3(CO)_9C$ cluster bears an apically C-bonded CS_2 group, the sulfur atoms of which are symmetrically bonded to two cobalt atoms of a $Co_3(CO)_7S$ unit, viz., *sym*-$Co_6(CO)_{16}C_2S_3$[2] (V).[3] This compound is structurally closely related to two other hexacobalt complexes which were observed some time ago as the first polynuclear CS_2 derivatives of cobalt carbonyl.[4,5] These two compounds were formulated initially as two isomers (Ia and Ib[3]) of "$Co_4(CO)_{10}CS_2$"[4,5] on the basis of their virtually identical elemental analyses; since molecular weight determinations proved unsuccessful, the tetracobalt formulas were believed to account correctly for the observed Co/S ratio of 2 and at the same time also for the occurrence of IR absorption bands in the 1100–700-cm^{-1} region, which suggested the presence of coordinated CS_2 in these molecules.



V



Ia



Ib

Subsequently their hexanuclear geometries were established by preliminary X-ray diffraction analyses.[6,7] As a common feature in both cases a CS_2 unit was found to bridge, in different manners, a $SCo_3(CO)_7$ fragment (derived from a $SCo_3(CO)_9$ molecule[8] by the loss of two equatorial CO groups) with another tricobalt entity. (The extra sulfur atom in the Co_3S cluster unit accounts for the Co/S ratio of 2 in these hexacobalt complexes.)

Like the new complex V, Ia also has the composition $Co_6(CO)_{16}C_2S_3$. However, in the case of Ia the CS_2 linkage is arranged in an asymmetric manner so that the apical C atom of the $CCo_3(CO)_9$ unit is bonded to a sulfur atom of CS_2 and the carbon and second sulfur atom of it are bonded to two Co atoms of the Co_3S pyramid, so that a four-membered Co_2CS ring is formed. Hence the molecule of Ia is completely asymmetric and chiral.[6]

The molecule of Ib, however, contains the CS_2 entity in a symmetric array, and as in V, a symmetric five-membered Co_2S_2C ring is the result of the symmetric chelate bonding of the two sulfur atoms to the Co_3S unit.[7] These two com-

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(1) (a) University of Turin. (b) ETH, Zurich.

(2) P. L. Stanghellini, G. Gervasio, R. Rossetti, and G. Bor, *J. Organomet. Chem.*, **187**, C37 (1980).

(3) We maintain the same labeling of the Co–CO–CS_2 complexes as applied in most of our earlier papers on this topic,[2,5] for sake of consistency and of simpler cross-references.

(4) L. Markó, G. Bor, and E. Klumpp, *Angew. Chem.*, **75**, 248 (1963).

(5) E. Klumpp, G. Bor, and L. Markó, *J. Organomet. Chem.*, **11**, 207 (1968).

(6) C. H. Wei, (a) *Annu. Prog. Rep.—Oak Ridge Natl. Lab., Biol. Div.*, 325 (1967); (b) personal communication, 1976.

(7) J. F. Blount and L. F. Dahl, unpublished results (personal communication, 1969).

(8) (a) L. Markó, G. Bor, and E. Klumpp, *Chem. Ind.* (*London*), 1491 (1961); (b) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967).

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Table I. Experimental and Crystal Data for X-ray Analysis[a]

	$[Co_3(CO)_9C]CS_2$-$[Co_3(CO)_7S]$ (V)	$[Co_3(CO)_8]CS_2$-$[Co_3(CO)_7S]$ (Ib)
space group	$P\bar{1}$, ($C_1{}^1$, No. 2)	
a, Å	12.822 (4)	14.131 (4)
b, Å	13.399 (4)	10.580 (4)
c, Å	8.851 (4)	9.768 (4)
α, deg	100.07 (4)	95.58 (3)
β, deg	85.72 (3)	83.83 (3)
γ, deg	106.20 (4)	111.33 (4)
V, Å^3	1437.2	1349.8
mol wt	922.0	881.9
Z	2	
ρ(calcd), g cm^{-3}	2.13	2.17
μ(Mo Kα), cm^{-1}	35.3	37.5
approx cryst dimens, mm	0.05 × 0.36 × 0.18	0.10 × 0.24 × 0.32
rel transmission factor	0.554/0.994	0.769/0.998
diffractometer	Philips PW 1100 (cryst sealed in Lindemann glass capillaries)	
radiation	Mo Kα (graphite monochromatized, $\lambda = 0.7107$ Å)	
scan technique	θ-2θ	
scan width, deg	1.50	
scan speed, deg s^{-1}	0.05	
scan range (θ), deg	2.0-22.0	2.0-25.0
bkgd	each bkgd measd for 5 s	
stds (hkl) (measd every 240 reflctns)	(500), (050), (003)	(600), (150), (206)
collected reflctns	3543	4754
reflctns with $I > 3\sigma(I)$	3224	3730
final R	0.066	0.023
final R_w	0.070	0.024

[a] In this and the subsequent tables the esd's are in parentheses.

pounds are hence the first examples of complexes where a symmetric bidentate S,S-bonded XCS_2 unit bridges "diequatorially" over a directly bonded metal–metal fragment. Only one similar structural unit containing a five-membered M_2S_2C ring has been reported so far, viz., (μ-H)(μ-HCS_2)-$Os_3(CO)_{10}$ and its phenyldimethylphosphine derivative.[9] However, this contains the sulfur atoms in "diaxial" coordination relative to the M_3 plane.

Hence a detailed structural comparison of V and Ib seemed very attractive. Since the details of the older X-ray study on Ib[7] were not available, this analysis was now repeated contemporaneously with the refinement of the structure of V. This paper reports on these results. The X-ray analysis of further cluster compounds formed in this reaction is in progress.[10] A comprehensive discussion of the reaction of $Co_2(CO)_8$ with CS_2 will be given after the full characterization of all products.

Experimental Section

Preparation of the Complexes. The two products have been prepared by reacting $Co_2(CO)_8$ with CS_2 at room temperature, as reported before.[2,5] The best yield (V, ca. 15%; Ib, ca. 20–25%, based on the soluble carbonyl complexes, which are, in total, ca. 15% of the starting $Co_2(CO)_8$) is obtained with use of a molar ratio of $Co_2(CO)_8/CS_2$ of ca. 1/4. The TLC of the reaction mixture (adsorbent Kieselgel 60 PF, Merck; eluent petroleum ether) shows the two complexes as a dark brown band, not well resolved, near the bottom of the plate. The purification requires subsequent TLC operations and/or extraction of the more soluble complex V by petroleum ether from the mixed crystals. Good crystals suitable for X-ray measurement are finally obtained from hydrocarbon solution at −20 °C. Both compounds are black solids, stable in air and soluble in chloroform or carbon tetrachloride; the solutions are fairly stable and should be stored under inert atmosphere.

Table II. Fractional Atomic Coordinates Referred to One Molecule for $[Co_3(CO)_9C]CS_2[Co_3(CO)_7S]$ (V)

atom	x/a	y/b	z/c
Co(1)	0.7847 (1)	0.8031 (1)	−0.1515 (2)
Co(2)	0.8302 (1)	0.7166 (1)	0.0499 (2)
Co(3)	0.7809 (1)	0.6154 (1)	−0.2088 (2)
Co(4)	1.2148 (1)	0.8346 (1)	−0.4283 (2)
Co(5)	1.2600 (1)	0.7484 (1)	−0.2256 (2)
Co(6)	1.3791 (1)	0.7633 (1)	−0.4664 (2)
C(1)	0.846 (1)	0.936 (1)	−0.058 (1)
C(2)	0.789 (1)	0.830 (1)	−0.343 (2)
C(3)	0.642 (1)	0.793 (1)	−0.101 (2)
C(4)	0.909 (1)	0.827 (1)	0.175 (2)
C(5)	0.884 (1)	0.621 (1)	0.110 (2)
C(6)	0.701 (1)	0.693 (1)	0.156 (2)
C(7)	0.788 (1)	0.605 (1)	−0.417 (2)
C(8)	0.834 (1)	0.506 (1)	−0.197 (2)
C(9)	0.636 (1)	0.558 (1)	−0.173 (2)
C(10)	1.199 (1)	0.856 (1)	−0.617 (2)
C(11)	1.271 (1)	0.969 (1)	−0.337 (2)
C(12)	1.300 (1)	0.650 (1)	−0.151 (1)
C(13)	1.325 (1)	0.864 (1)	−0.097 (2)
C(14)	1.400 (1)	0.767 (1)	−0.669 (2)
C(15)	1.457 (1)	0.672 (1)	−0.448 (2)
C(16)	1.472 (1)	0.884 (1)	−0.385 (2)
C(17)	0.896 (1)	0.736 (1)	−0.145 (1)
C(18)	1.010 (1)	0.758 (1)	−0.201 (1)
O(1)	0.885 (1)	1.018 (1)	−0.002 (1)
O(2)	0.786 (1)	0.852 (1)	−0.469 (1)
O(3)	0.553 (1)	0.786 (1)	−0.072 (1)
O(4)	0.958 (1)	0.896 (1)	0.259 (1)
O(5)	0.915 (1)	0.560 (1)	0.155 (1)
O(6)	0.621 (1)	0.684 (1)	0.225 (1)
O(7)	0.789 (1)	0.602 (1)	−0.544 (1)
O(8)	0.860 (1)	0.433 (1)	−0.185 (1)
O(9)	0.548 (1)	0.522 (1)	−0.151 (1)
O(10)	1.192 (1)	0.871 (1)	−0.737 (1)
O(11)	1.308 (1)	1.054 (1)	−0.283 (1)
O(12)	1.329 (1)	0.588 (1)	−0.105 (1)
O(13)	1.365 (1)	0.938 (1)	−0.013 (1)
O(14)	1.405 (1)	0.768 (1)	−0.796 (1)
O(15)	1.504 (1)	0.614 (1)	−0.438 (1)
O(16)	1.533 (1)	0.959 (1)	−0.336 (1)
S(1)	1.0418 (3)	0.8235 (3)	−0.3525 (4)
S(2)	1.0964 (2)	0.7188 (2)	−0.1067 (4)
S(3)	1.2107 (3)	0.6715 (2)	−0.4519 (4)

Collection and Reduction of X-ray Data. The values of the cell parameters and the main experimental data for the structure determination are reported in Table I. The lattice parameters were obtained from the refinement of 25 θ angles. No significant decrease in the intensities of the three standard reflections was detected. The adsorption correction was applied with use of the method previously reported.[11] Secondary extinction correction has not been made.

Solution and Refinement of the Structures. The three-dimensional Patterson map was interpreted in terms of six independent heavy-atom positions in the centric space group $P\bar{1}$, and the subsequent refinement confirmed the choice. All the other atoms were localized from subsequent series of difference-Fourier syntheses. Only the reflections with $I > 3\sigma(I)$ were taken into account and used for least-squares refinement. The weighting scheme was

$$w = 1/(\sigma(F)^2 + aF^2)$$

where a was varied, in order to maintain $\sum w\Delta^2$ satisfactorily constant for the amplitudes batched in various ranges of $|F_o|$. In the last least-squares cycles all the atoms were anisotropically refined; for the solution and refinement of the structure the programs of SHELX 76[12] were used. The calculation of the best planes passing through the atoms was made by the method of ref 13. A list of observed and calculated structure factors and of thermal anisotropic parameters is available.[14] Final fractional coordinates are listed in Tables II and

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(9) R. D. Adams and J. P. Selegue, *J. Organomet. Chem.*, **195**, 223 (1980).

(10) P. L. Stanghellini, G. Gervasio, R. Rossetti, and G. Bor, *Int. Conf. Organomet. Chem.*, *10th*, 91 (1981).

(11) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **A24**, 351 (1968).

(12) G. M. Sheldrick, "SHELX 76, A System of Computer Programs", Cambridge University, Cambridge, England, 1976.

(13) V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959).

(14) Supplementary material.

Table III. Fractional Atomic Coordinates Referred to One Molecule for $[Co_3(CO)_8]CS_2[Co_3(CO)_7S]$ (Ib)

atom	x/a	y/b	z/c
Co(1)	0.67384 (4)	0.27426 (4)	0.80311 (5)
Co(2)	0.63758 (4)	0.33249 (4)	0.58381 (4)
Co(3)	0.50358 (4)	0.29036 (4)	0.78047 (5)
Co(4)	0.84403 (3)	0.65769 (4)	0.89379 (4)
Co(5)	0.81241 (3)	0.71682 (4)	0.66563 (5)
Co(6)	0.99090 (4)	0.81111 (5)	0.74589 (5)
C(1)	0.6324 (3)	0.1508 (4)	0.9302 (4)
C(2)	0.8033 (3)	0.2790 (4)	0.7758 (4)
C(3)	0.6331 (3)	0.1628 (4)	0.6377 (4)
C(4)	0.5445 (3)	0.2797 (4)	0.4594 (4)
C(5)	0.7495 (4)	0.3600 (5)	0.4675 (5)
C(6)	0.4702 (3)	0.2900 (4)	0.9650 (4)
C(7)	0.4244 (3)	0.3766 (4)	0.7282 (4)
C(8)	0.4206 (3)	0.1132 (4)	0.7354 (4)
C(9)	0.9014 (3)	0.5990 (4)	1.0203 (4)
C(10)	0.8049 (3)	0.7796 (4)	1.0013 (4)
C(11)	0.8372 (3)	0.7451 (4)	0.4842 (4)
C(12)	0.7654 (3)	0.8519 (4)	0.7271 (4)
C(13)	1.0628 (3)	0.8703 (4)	0.5852 (5)
C(14)	1.0909 (3)	0.8014 (4)	0.8425 (5)
C(15)	0.9772 (3)	0.9675 (4)	0.8196 (4)
C(16)	0.6308 (2)	0.4423 (3)	0.7765 (3)
O(1)	0.6093 (3)	0.0708 (4)	1.0076 (4)
O(2)	0.8823 (2)	0.2766 (3)	0.7594 (4)
O(3)	0.6181 (3)	0.0520 (3)	0.5941 (3)
O(4)	0.4860 (3)	0.2444 (3)	0.3807 (4)
O(5)	0.8186 (3)	0.3773 (5)	0.3924 (4)
O(6)	0.4501 (2)	0.2911 (3)	1.0802 (3)
O(7)	0.3748 (3)	0.4323 (4)	0.7010 (4)
O(8)	0.3679 (3)	0.0081 (3)	0.7093 (3)
O(9)	0.9323 (3)	0.5585 (4)	1.0001 (4)
O(10)	0.7814 (2)	0.8567 (3)	1.0715 (3)
O(11)	0.8546 (3)	0.7636 (4)	0.3708 (3)
O(12)	0.7370 (2)	0.9362 (3)	0.7669 (3)
O(13)	1.1073 (4)	0.9106 (4)	0.4861 (4)
O(14)	1.1524 (3)	0.7925 (4)	0.9015 (4)
O(15)	0.9695 (2)	1.0660 (3)	0.8640 (3)
S(1)	0.6954 (1)	0.4832 (1)	0.9270 (1)
S(2)	0.6551 (1)	0.5571 (1)	0.6493 (1)
S(3)	0.9031 (1)	0.5987 (1)	0.6958 (1)

III for complexes V and Ib, respectively.

Description of the Structures and Discussion

The idealized molecular geometry of both complexes belongs to the point group C_s, with a mirror plane defined by the core atoms Co(6), S(3), C(18), C(17), and Co(3) (complex V) and by the atoms Co(6), S(3), C(16), and Co(3) and the bridging CO group (complex Ib) (cf. Figures 1–3). The structures can be described as being formed by a Co_3S and a Co_3C cluster linked by a CS_2 bridge; the S atoms are thought to substitute two equatorial CO's of the $Co_3S(CO)_9$ parent molecule.[8b] The most significant difference between the two structures is in that the C atom of the CS_2 bridge is linked to the apical C atom of the Co_3C cluster in complex V, whereas in complex Ib this atom *is itself* the apical atom of the Co_3C unit. So in the last case the binding of the CS_2 bridge seems unprecedented in the respect that the two sulfur atoms are bonded also to two cobalt atoms which bear only two terminal CO's each and one μ-CO bridge. Some relevant distances and angles are listed in Tables IV and V for complexes V and Ib, respectively.[14]

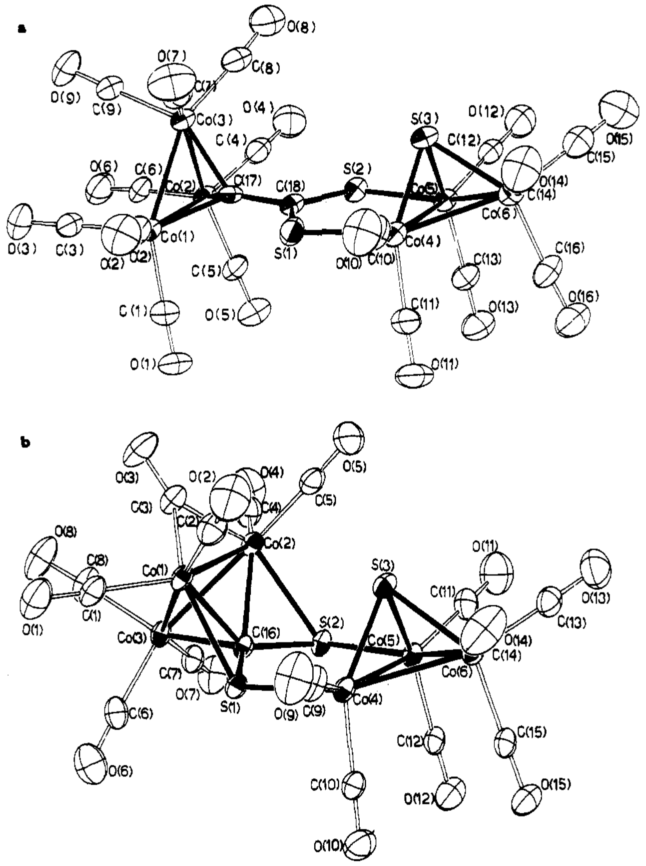

Figure 1. Perspective ORTEP plots in approximately identical orientations with respect to the CS_2Co_2 pentagons (30% probability ellipsoids): (a) $Co_6(CO)_{16}C_2S_3$ (V); (b) $Co_6(CO)_{15}CS_3$ (Ib).

The Co_3S Cluster. An increasing number of carbonyl clusters that contain the pyramidal Co_3S unit has been reported (Table VI). Some of them show an idealized local C_{3v} sym-

Table IV. Selected Values of Interatomic Distances (Å) and Angles (Deg) of $[Co_3(CO)_9C]CS_2[Co_3(CO)_7S]$ (V)

Co(1)–Co(2)	2.473 (2)	Co(4)–Co(5)	2.478 (2)	Co(5)–S(3)	2.140 (3)
Co(1)–Co(3)	2.464 (2)	Co(4)–Co(6)	2.524 (2)	Co(6)–S(3)	2.173 (4)
Co(1)–C(17)	1.896 (10)	Co(4)–S(1)	2.242 (4)	C(17)–C(18)	1.478 (16)
Co(2)–Co(3)	2.476 (2)	Co(4)–S(3)	2.146 (3)	C(18)–S(1)	1.696 (11)
Co(2)–C(17)	1.890 (12)	Co(5)–Co(6)	2.531 (2)	C(18)–S(2)	1.674 (10)
Co(3)–C(17)	1.886 (11)	Co(5)–S(2)	2.241 (4)		
Co(2)–Co(1)–Co(3)	60.2 (1)	C(10)–Co(4)–S(1)	95.0 (5)	Co(1)–C(17)–Co(2)	81.6 (5)
Co(2)–Co(1)–C(17)	49.1 (4)	C(11)–Co(4)–S(1)	96.7 (4)	Co(1)–C(17)–Co(3)	81.3 (4)
Co(3)–Co(1)–C(17)	49.2 (3)	S(1)–Co(4)–S(3)	99.2 (1)	Co(1)–C(17)–C(18)	133.2 (8)
Co(1)–Co(2)–Co(3)	59.7 (1)	Co(4)–Co(5)–Co(6)	60.5 (1)	Co(2)–C(17)–Co(3)	82.0 (5)
Co(1)–Co(2)–C(17)	49.3 (3)	Co(4)–Co(5)–S(2)	96.4 (1)	Co(2)–C(17)–C(18)	132.1 (8)
Co(3)–Co(2)–C(17)	49.0 (3)	Co(4)–Co(5)–S(3)	54.8 (1)	Co(3)–C(17)–C(18)	127.6 (8)
Co(1)–Co(3)–Co(2)	60.1 (1)	Co(6)–Co(5)–S(2)	151.2 (1)	C(17)–C(18)–S(1)	116.2 (8)
Co(1)–Co(3)–C(17)	49.5 (3)	Co(6)–Co(5)–S(3)	54.7 (1)	C(17)–C(18)–S(2)	117.5 (8)
Co(2)–Co(3)–C(17)	49.1 (4)	C(12)–Co(5)–S(2)	95.2 (4)	S(1)–C(18)–S(2)	126.3 (7)
Co(5)–Co(4)–Co(6)	60.8 (1)	C(13)–Co(5)–S(2)	96.9 (4)	Co(4)–S(1)–C(18)	109.4 (4)
Co(5)–Co(4)–S(1)	97.1 (1)	S(2)–Co(5)–S(3)	98.8 (1)	Co(5)–S(2)–C(18)	110.4 (4)
Co(5)–Co(4)–S(3)	54.6 (1)	Co(4)–Co(6)–Co(5)	58.7 (1)	Co(4)–S(3)–Co(5)	70.7 (1)
Co(6)–Co(4)–S(1)	152.1 (1)	Co(4)–Co(6)–S(3)	53.7 (1)	Co(4)–S(3)–Co(6)	71.5 (1)
Co(6)–Co(4)–S(3)	54.8 (1)	Co(5)–Co(6)–S(3)	53.5 (1)	Co(5)–S(3)–Co(6)	71.9 (1)

Table V. Selected Values of Interatomic Distances (Å) and Angles (Deg) for $[Co_3(CO)_8]CS_2[Co_3(CO)_7S]$ (Ib)

Co(1)–Co(2)	2.440 (1)	Co(2)–C(16)	2.126 (3)	Co(4)–S(3)	2.150 (1)
Co(1)–Co(3)	2.507 (1)	Co(2)–S(2)	2.330 (1)	Co(5)–Co(6)	2.533 (1)
Co(1)···Co(4)	3.961 (1)	Co(3)···C(3)	2.828 (4)	Co(5)–S(2)	2.261 (1)
Co(1)–C(16)	2.123 (3)	Co(3)–C(16)	1.927 (3)	Co(5)–S(3)	2.147 (1)
Co(1)–S(1)	2.348 (1)	Co(4)–Co(5)	2.499 (1)	Co(6)–S(3)	2.172 (1)
Co(2)–Co(3)	2.499 (1)	Co(4)–Co(6)	2.528 (1)	C(16)–S(1)	1.748 (3)
Co(2)···Co(5)	3.970 (1)	Co(4)–S(1)	2.253 (1)	C(16)–S(2)	1.743 (3)
Co(2)–Co(1)–Co(3)	60.7 (0)	Co(6)–Co(4)–S(1)	153.6 (0)	Co(1)–C(16)–Co(3)	76.3 (1)
Co(2)–Co(1)–C(16)	55.0 (1)	Co(6)–Co(4)–S(3)	54.6 (0)	Co(1)–C(16)–S(1)	73.9 (1)
Co(2)–Co(1)–S(1)	97.9 (0)	C(9)–Co(4)–S(1)	91.3 (1)	Co(1)–C(16)–S(2)	135.5 (2)
Co(3)–Co(1)–C(16)	48.3 (1)	C(10)–Co(4)–S(1)	95.3 (1)	Co(2)–C(16)–Co(3)	76.0 (1)
Co(3)–Co(1)–S(1)	80.2 (0)	S(1)–Co(4)–S(3)	102.0 (0)	Co(2)–C(16)–S(1)	137.4 (2)
C(16)–Co(1)–S(1)	45.7 (1)	Co(4)–Co(5)–Co(6)	60.3 (0)	Co(2)–C(16)–S(2)	73.3 (1)
Co(1)–Co(2)–Co(3)	61.0 (0)	Co(4)–Co(5)–S(2)	97.2 (0)	Co(3)–C(16)–S(1)	116.7 (2)
Co(1)–Co(2)–C(16)	54.9 (1)	Co(4)–Co(5)–S(3)	54.5 (0)	Co(3)–C(16)–S(2)	118.1 (2)
Co(1)–Co(2)–S(2)	97.3 (0)	Co(6)–Co(5)–S(2)	154.0 (0)	S(1)–C(16)–S(2)	122.4 (2)
Co(3)–Co(2)–C(16)	48.4 (1)	Co(6)–Co(5)–S(3)	54.6 (0)	Co(1)–S(1)–Co(4)	118.8 (0)
Co(3)–Co(2)–S(2)	81.3 (0)	C(11)–Co(5)–S(2)	95.8 (1)	Co(1)–S(1)–C(16)	60.3 (1)
C(16)–Co(2)–S(2)	45.8 (1)	C(12)–Co(5)–S(2)	94.2 (1)	Co(4)–S(1)–C(16)	110.0 (1)
Co(1)–Co(3)–Co(2)	58.3 (0)	S(2)–Co(5)–S(3)	102.7 (0)	Co(2)–S(2)–Co(5)	119.7 (0)
Co(1)–Co(3)–C(16)	55.4 (1)	Co(4)–Co(6)–Co(5)	59.2 (0)	Co(2)–S(2)–C(16)	60.9 (1)
Co(2)–Co(3)–C(16)	55.6 (1)	Co(4)–Co(6)–S(3)	53.8 (0)	Co(5)–S(2)–C(16)	109.5 (1)
Co(5)–Co(4)–Co(6)	60.5 (0)	Co(5)–Co(6)–S(3)	53.6 (0)	Co(4)–S(3)–Co(5)	71.1 (0)
Co(5)–Co(4)–S(1)	97.1 (0)	C(13)–Co(6)–S(3)	103.9 (1)	Co(4)–S(3)–Co(6)	71.6 (0)
Co(5)–Co(4)–S(3)	54.4 (0)	Co(1)–C(16)–Co(2)	70.1 (1)	Co(5)–S(3)–Co(6)	71.8 (0)

Table VI. Some Relevant Features of $Co_3(CO)_xS$ Clusters ($x = 6$–9)

	Co–Co, Å		Co–S_{ap}, Å		ref
$Co_3(CO)_9S$	2.633 (7)	2.612 (6)	2.143 (10)	2.147 (10)	8b
	2.649 (7)	2.627 (7)	2.131 (10)	2.122 (9)	
	2.655 (5)	2.641 (6)	2.141 (10)	2.148 (10)	
$[Co_3(CO)_6S]_2(\mu_6\text{-}C)$	2.433 (2)	2.435 (2)	2.195 (3)	2.203 (3)	26, 27
	2.433 (2)	2.433 (2)	2.181 (3)	2.184 (3)	
	2.428 (2)	2.431 (2)	2.197 (3)	2.191 (3)	
sym-$[Co_3(CO)_9C]CS_2[Co_3(CO)_7S]$	2.478 (2)		2.173 (4)		this work
	2.524 (2)		2.146 (3)		
	2.531 (2)		2.140 (3)		
$[Co_3(CO)_8]CS_2[Co_3(CO)_7S]$	2.499 (1)		2.172 (1)		this work
	2.528 (1)		2.150 (1)		
	2.533 (1)		2.147 (1)		
$[SCo_3(CO)_7]_2S_2$	2.485 (10)	2.463 (10)	2.160 (13)	2.134 (12)	15
	2.524 (9)	2.531 (12)	2.162 (12)	2.122 (12)	
	2.521 (12)	2.544 (9)	2.152 (14)	2.139 (12)	
asym-$[Co_3(CO)_9C]CS_2[Co_3(CO)_7S]$	2.427		2.18		6[a]
	2.533		2.16		
	2.559		2.15		
$SCo_6(CO)_{11}(SC_2H_5)_4$	2.459 (7)		2.16 (1)		16
	2.450 (7)		2.17 (1)		
	2.471 (8)		2.16 (1)		
$(CH_3CNC_6H_{11})Co_3(CO)_7S$	2.416 (0)		2.172 (1)		18
	2.554 (0)		2.147 (1)		
	2.538 (0)		2.158 (1)		
$(CSNMe_2)Co_3(CO)_7S$	2.440 (1)		2.168 (2)		17
	2.549 (1)		2.148 (2)		
	2.525 (1)		2.145 (2)		

[a] δ values are 0.004–0.007 Å for the Co–Co bonds and 0.01–0.02 Å for the Co–S bonds.[6b]

metry with three identical (within the limits of error) Co–Co and Co–S bonds. Others have a Co–Co bond bridged by two or three atoms, so forming a 4- or 5-membered ring; the bridge gives rise to a deformation of the cluster, thereby reducing the length of the bridged bond and moving it toward the apical sulfur atom. In the compounds dealt with in the present study the unique Co–Co bond is decreased by ca. 0.03 (V) and 0.05 Å (Ib), and as expected this decrease is less evident than the one in the 4-membered ring complexes (ca. 0.06 Å (average) in $[SCo_3(CO)_7]_2S_2$,[15] ca. 0.10 Å in *asym*-$Co_6(CO)_{16}C_2S_3$,[6] and $SCo_3(CO)_7(CSNMe_2)$,[17] and 0.12 and 0.14 Å, respectively, in $SCo_3(CO)_7(MeCNC_6H_{11})$[18]).

Compounds V and Ib show a slight but significant displacement of the apical sulfur atom away from the equidistant Co–S position. For V this relative increase of the unique Co–S bond (average 0.030 Å) is even greater than the one observed by Patin et al.[18] for the μ-imino derivative of $SCo_3(CO)_9$ (i.e., average 0.020 Å). (The large σ value reported[15] does not allow the observation of any difference of this kind in $[SCo_3(CO)_7]_2S_2$.) The position of the CO groups does not vary greatly with respect to the reference structure of $Co_3(CO)_9S$,[8b] and the S atoms of the bridge occupy almost exactly the

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(16) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **90**, 3977 (1968).

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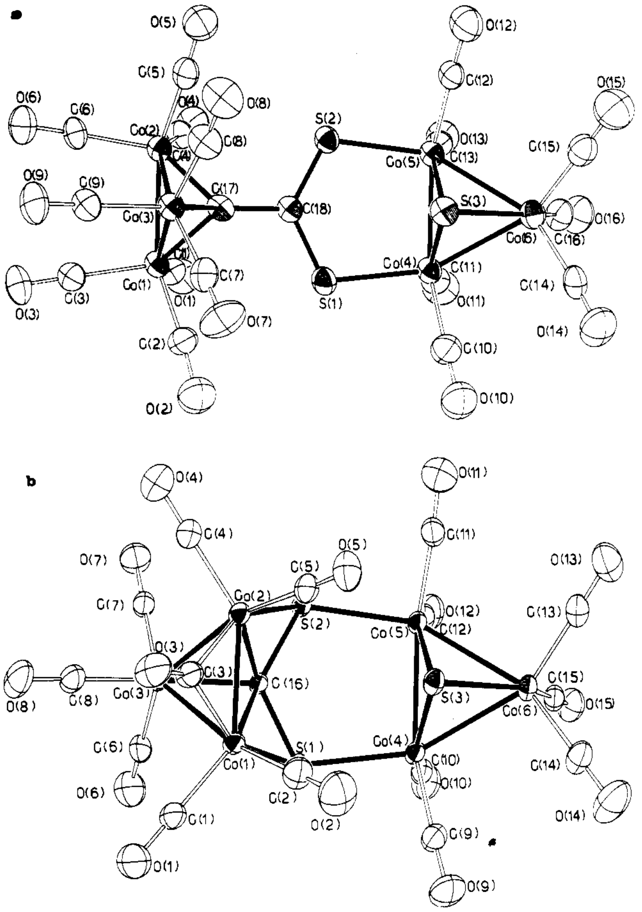

Figure 2. Top views normal to the CS_2Co_2 planes (30% probability ellipsoids): (a) $Co_6(CO)_{16}C_2S_3$ (V); (b) $Co_6(CO)_{15}CS_3$ (Ib) (view ca. 3° off normal, to reduce the overlap of atom Co(3) by O(3)).

position of two equatorial CO's (Co–Co–S_{eq} angles 96.7° (average) for V and 97.1° (average) for Ib vs. 96.5° for Co–Co–CO_{eq} of $Co_3(CO)_9S$). The equatorial CO's are tilted toward the S atoms, and the angles of the Co–CO_{eq} directions with the Co_3 plane are in the 13–16° range for both the compounds, in good agreement with the corresponding values of $Co_3(CO)_9S$ (16°). A slight closing of the CO–Co–S_{eq} angles with respect to the CO–Co(6)–CO values (94.1 (average) vs. 100.7° (average) in Ib, 95.9° (average) vs. 100.2° (average) in V) indicates a small attractive interaction between the CO's and the ring S atoms that does not influence the CO–Co–CO angles. Similar observation is not possible for $[Co_3(CO)_7S]_2S_2$ since its geometry is largely distorted by the short $-S_{eq}-S_{eq}-$ bridge.[15]

The Co_3C Cluster. Complex V shows a Co_3C cluster where the bond distances and angles lie in the range of typical $Co_3(CO)_9CR$ complexes.[19] The arrangement of the carbonyl groups is not affected by the other part of the molecule: e.g., the dihedral angle between the plane defined by a cobalt atom and its two equatorial carbon atoms and the plane of the Co_3 triangle is 28° (average), very similar to the mean value of $[(CO)_9Co_3C]_2C_2$ (28°),[20] of $CH_3CCo_3(CO)_9$ (29°),[21] and of the whole $RCCo_3(CO)_9$ series (30°),[22,23] and none of the $Co(CO)_3$ entities is forced to torsional displacements by repulsive interaction with the bulky "substitutent" R = $(CS_2$-$Co_3(CO)_7S)$, in contrast, e.g., to the R = mesityl[24] and benzoyl[25] derivatives. Also the Co–C(17)–C(18) angles are rather regular: the slight decrease of the angle Co(3)–C(17)–C(18) (127.6°) and the corresponding increase of the other two angles (132.1 and 133.2°; the average calculated for 27 reported $RCCo_3(CO)_9$ structures[22] is 131.5°) indicates a corresponding slight tilting of the entire $(CO)_9Co_3C$ unit.

On the other hand, in complex Ib, the unusual bonding conditions of the CS_2 bridge (vide infra) and the presence of a bridging carbonyl group cause a significant distortion of the Co_3C cluster. First, the Co_3 triangle is isosceles, the unique bond (2.440 Å) being one of the shortest Co–Co single bonds observed in Co_3C units, and it is similar to that of the triangular faces of the elongated Co_6C prism in $Co_6C(CO)_{12}S_2$[26,27] (2.432 Å) or to the triply bridged Co–Co edge of a perfluorobis(arsino) derivative of the Co_3C cluster.[28] The other two Co–Co bonds are longer (2.503 Å (average)). Further, the apical carbon atom is removed from the symmetric position: the C–Co(3) distance (1.927 Å) lies in the usual range of the Co_3C cores, whereas the other two are remarkably longer (2.125 Å (average)) and are similar to the Co–C distance when the C atom is part of a π-donor ring. The carbonyl groups maintain the usual local geometry around the cobalt atoms; i.e., the CO–Co–CO angles have quite normal values (93–101°). However, the two $Co(1)(CO)_2$ and $Co(2)(CO)_2$ units are greatly rotated with respect to the Co_3 plane, probably because of the effect of the CS_2 ligand, so the equatorial C(2) and C(5) atoms lie practically on the Co_3 plane and CO(1) and CO(4) are tilted on the opposite side of the same plane (see Figure 4).[29] As a consequence, a CO group of each $Co(CO)_3$ unit collapses in a unique axial CO, bridging the two cobalt atoms. The axial CO bridge is unusual in the metal carbonyl clusters: only few examples have previously been reported for Co_3 clusters.[24,30,31]

The CS_2 Ligand. In both complexes the CS_2 ligand forms a pentaatomic ring with two Co atoms of the Co_3S cluster, and in some aspects the two rings are similar (Co–Co–S angles 96.7° (average) (V) and 97.1° (average) (Ib), Co–S–C angles 109.9° (average) (V) and 109.7° (average) (Ib), Co–S distances 2.241 Å (average) (V) and 2.257 Å (average) (Ib), Co–Co distances 2.478 Å (V) and 2.499 Å (Ib)). From other points of view the rings are markedly different: the S–C–S angle is larger in V (126.3°) than in Ib (122.4°) and especially the C–S bonds are shorter in V (1.685 Å (average)) than in Ib (1.745 Å (average)), indicating a greater double-bond character (33% (average) vs. 19% (average)) according to Abrahams.[32] As a consequence, the ring in V shows quite a good planarity, whereas in Ib it is puckered.[14] This deformation is not unexpected because of the much greater constraint of the CS_2 ligand, as is implied in a multiple bond with

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(22) Calculated with the program GEOM78[23] from 25 compounds registered in the Cambridge Crystallographic Database[23] plus two novel structures reported recently.[24]

(23) Cambridge Crystallographic Database, Cambridge Crystallographic Data Center, July 1979; version for the CDC computer of ETH Zurich by B. Schweizer.

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(29) The values of the most significant angles are as follows: 27° for the dihedral angle between the mean plane passing through Co(3), CO(6), and CO(7) and the Co_3 plane; 1 and 2°, respectively, between the Co(1)–CO(2) and Co(2)–CO(5) directions and the Co_3 plane; 29 and 28°, respectively, between the Co(1)–CO(1) and Co(2)–CO(4) directions and the Co_3 plane.

(30) T. W. Matheson and B. R. Penfold, *Acta Crystallogr., Sect. B*, **B33**, 1980 (1977).

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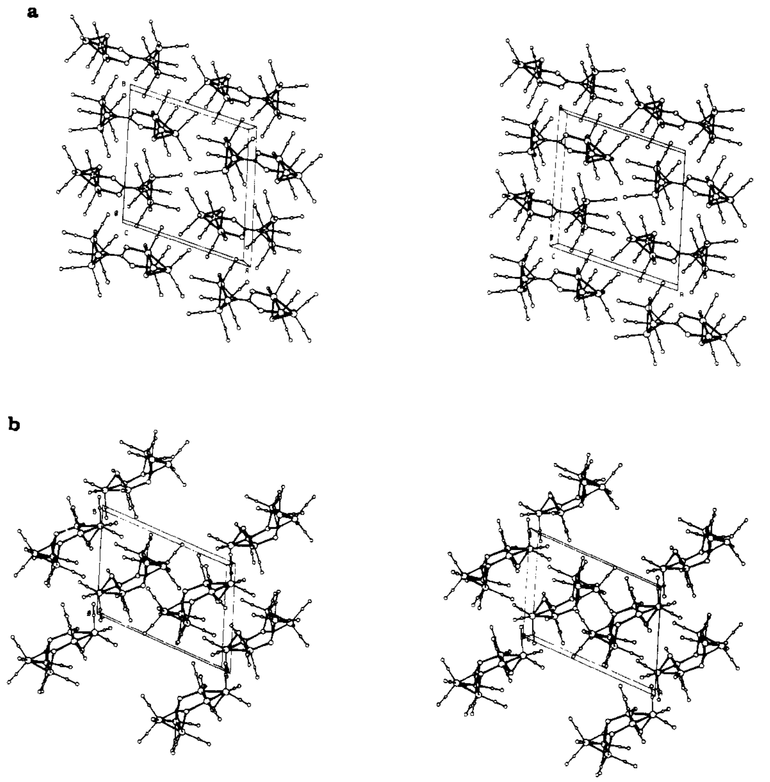

Figure 3. Stereoscopic PLUTO drawings[23] of the elementary cells and their contents, including their neighborhood within −0.5 and +1.5 cell units along the axes *a* and *b*, with the view along axis *c*: (a) $Co_6(CO)_{16}C_2S_3$ (V); (b) $Co_6(CO)_{15}CS_3$ (Ib).

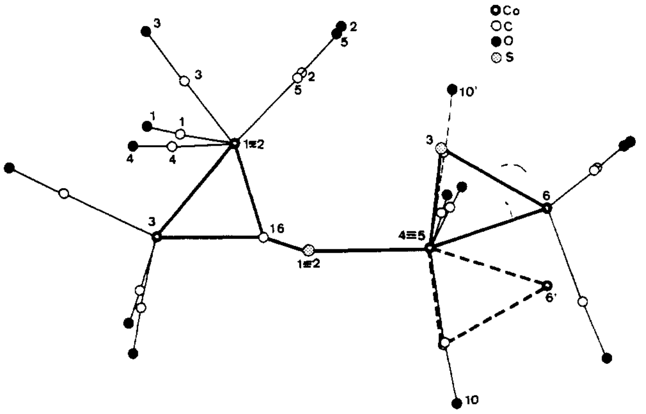

Figure 4. Schematic side view (normal to the idealized O(8)–C(8)–Co(3)–C(3)–O(3)–C(16)–S(3)–Co(6)–C(15)–O(15) plane) of complex Ib showing also the significant atoms of the $Co_3(CO)_7S$ fragment in its hypothetical "trans" orientation (cf. text).

the $Co_3(CO)_8$ group. The different C–S distances reflect the different ways of coordination of the CS_2 entity. In V the C–S value is similar to those shown by CS_2 σ bonded to one or two metal atoms, so forming four-membered[33] or five-membered[40] rings, whereas in Ib it agrees well with a structural framework in which CS_2 is involved in a σ, π interaction with metals.[42] In the same manner, Ib shows two different Co–S distances according to the different way of bonding, the σ bonds Co(4,5)–S(1,2) being ca. 0.08 Å shorter than the Co(1,2)–S(1,2) distances, which bear a substantial π interaction. An electron bookkeeping shows that CS_2 is an eight-electron donor in Ib but it donates only four electrons in V. In both cases three electrons are coinvolved in the bonding to the two cobalt atoms of the $Co_3(CO)_7S$ entity, but in V only one is donated to the $Co_3(CO)_9C$ cluster via the single C–C bond,[46] whereas in Ib five electrons should be involved in the bonding to the $Co_3(CO)_8$ unit. The five-electron donor CS_2 could be formally regarded as a heteroallylic ligand similar to the systems bonded to $M_3(CO)_9$ (M = Ru, Os) units.[48] However, the bonding

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(33) E.g.: 1.68 Å in $Mo_2(S_2COC_2H_5)_4X_2$ (X = I, Br);[34] 1.68 Å (average) in $PhCSSCu(PPh_3)_2$;[35] 1.70 Å (average) in $[Cl(Ph_3P)_2Pt(CS_2)Pt(PPh_3)_2]BF_4 \cdot 0.2CH_2Cl_2$;[36] 1.66 Å (average) in $Re(HCS_2)(CO)_2[P(C_6H_5)_3]_2$;[37] 1.69 Å in $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$;[38] 1.66 Å (average) in $Ru(S_2CH)_2[P(C_6H_5)_3]_2$.[39]

(34) F. A. Cotton, M. W. Extine, and R. H. Niswander, *Inorg. Chem.*, **17**, 694 (1978).

(35) A. Camus, N. Marsich, and G. Nardin, *J. Organomet. Chem.*, **188**, 389 (1980).

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(39) A. E. Kalinin, A. I. Gusev, and Y. T. Struchkov, *Zh. Strukt. Khim.*, **14**, 859 (1973).

(40) E.g.: 1.68 Å in $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$;[38] 1.65 Å in $H(S_2CH)Os_3(CO)_{10}$ and 1.66 Å in $H(S_2CH)Os_3(CO)_9[P(CH_3)_2C_6H_5]$;[9] 1.67 Å (average) in $[M_2(S_2CCH_3Ph)_4]$ (M = Ni, Pd).[41]

(41) M. Bonamico, G. Dessy, and V. Fares, *J. Chem. Soc., Dalton Trans.*, 2315 (1977).

(42) E.g.: 1.756 Å in $Fe_2(CO)_6C_2S(C_6H_5)_2$;[43] 1.73 Å (average) in $Mo_2(S_2COC_2H_5)_4X_2$ (X = I, Br);[34] 1.78 Å in $(SCH_2)SOs_3(CO)_9[P(CH_3)_2C_6H_5]$;[44] 1.75 Å in $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$.[45]

(43) G. N. Schrauzer, H. N. Rabinowitz, J. A. K. Frank, and I. C. Paul, *J. Am. Chem. Soc.*, **92**, 212 (1970).

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(46) The C_{ap}–C value (1.48 Å) lies near the average (1.49 Å) calculated for 15 reported structures.[23]

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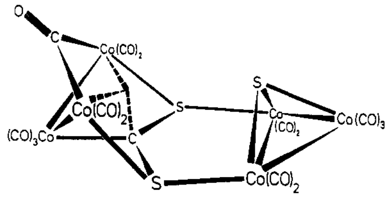


Figure 5. Structural scheme suggested by Blount and Dahl[7] for compound Ib.

relationships are decisively different in that in those structures the central ligand atom is within bonding distance only to one of the metal atoms, and in the isosceles M_3 triangle the unique metal–metal bond is longer than the other two. Moreover, the allylic ligand of the Ru_3 and Os_3 complexes forms a nearly planar five-membered ring with the two metal atoms joined by the long bond, whereas in Ib the ring is decisively distorted from planarity.[49] So CS_2 is able to form the partly closed cluster entity Co_3CS_2 in a way that has no resemblance to an allylic type bonding. Even if the Co(3)CS_2 entity is not completely planar but slightly pyramidal with the C atom at the vertex,[14] the bond angles between those bonds indicate that the five-coordinated carbon atom can be considered to be sp^2 bonded, with a little distortion, to Co(3) and to the two sulfur atoms. The two electrons of the p_z orbital may then interact with the Co(1)–Co(2) bond to form a bridge in a way not unlike the bonding mode of a bridging CO. The very reasonable Chini–Braterman three-center-bond interpretation of the bridging CO groups in di- and polynuclear carbonyls,[51] which implies also the "nonseparability" of these M–C and M–M bonds,[52] applies orbital overlap and bond angle arguments, which are straightforwardly applicable also for the Co(1)–C(16)–Co(2) bond system. Although the numerical value of this Co–C–Co angle (70.1°) is somewhat more acute than the Co–CO_{br}–Co angle (79.6°), this is a consequence of the longer Co–C(16) bonds, which, in turn, may represent a compromise between the requirements of the Co–S bond distances and the planarity of the sp^2 carbon atom. In this light, the small deviation of C(sp^2) from planarity is easily explained. Although, to our knowledge, the Braterman–Chini view of the bridging CO groups has not been questioned, the graphical representations of the CO-bridged structures continued to be drawn by ketone-like units with direct metal–carbon bonds.[53] Consequently we feel it is logical to invoke the same type of direct bonds also for the carbon atom of the bridging CS_2 group, since we fear that a drawing like the one in Figure 5 suggests an open ("butterfly"-like) Co_3 entity to the reader. In localized bond terms the bond orders of the two bridging Co–C(16) bonds appear to be considerably less than unity, as suggested by the notably (by 0.2 Å) longer bond length values, relative to that of the Co(3)–C(16) bond. In this light the Co_3S_2 framework could be regarded as a new type of semiclosed heavy-atom cluster of distorted-tetragonal-pyramidal structure, the atoms forming the base, Co(1), Co(2), S(1), and S(2), lying practically in a plane.[14] C(16) behaves as a semicarbidic carbon atom: its vibration frequencies (vide infra) support this point of view. Finally, if we consider the entire $Co_3(CO)_8CS_2$ group as equatorially bonded to the $Co_3(CO)_7S$ group (Ib), two geometrical arrangements are in principle possible, as shown in Figure 4. The "trans" form, S(3) trans to Co(1)–Co(2) with respect to Co(4)Co(5)S(2)S(1) plane (dashed line in the figure), is made unstable probably by the repulsion between the carbonyl groups. The same consideration applies to $[SCo_3(CO)_7]_2S_2$[15] but not to the complex V, owing to the possibility of rotation of the two Co_3 clusters around the C–C bond.

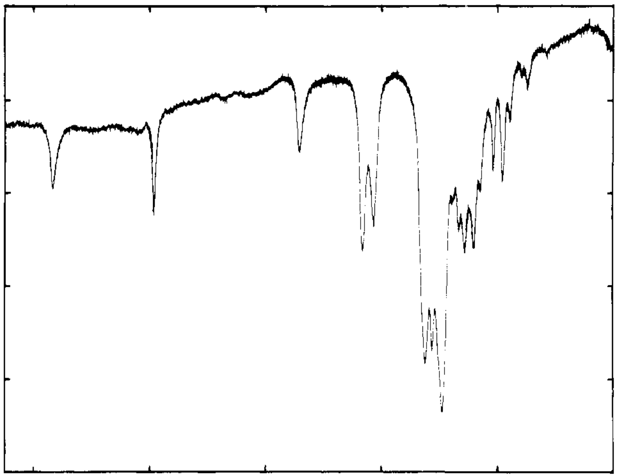


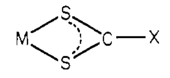
Figure 6. IR spectrum of $Co_6(CO)_{16}C_2S_3$ (V) in the 1250–200-cm^{-1} region (CsI pellet: 1.4 mg of sample/330 mg of CsI).

Infrared Spectra

1. Mid-IR Region. (a) $[(CO)_9Co_3C]CS_2[Co_3(CO)_7S]$ (V). There are three bands in the 1200–700-cm^{-1} region (Figure 6), and these undoubtedly arise from the vibrations of the CS_2 linking unit of the molecule. In this case the assignments can be made quite safely on a valence-bond basis since the "free floating" of the CS_2 group between the two Co_3E (E = C or S) cluster units does not imply a considerable coupling of the $\nu(C_{ap}–C)$ and the symmetric and antisymmetric ν(C–S) modes with other types of vibrations.

We assign the band at 1167 cm^{-1} to the C_{ap}–C stretching vibration. The same kind of vibration was found and assigned recently at 1163 cm^{-1} for $CH_3CCo_3(CO)_9$ and at 1182 cm^{-1} for the CD_3 derivative by Skinner et al.[54] The assignment is also evidenced by a normal-coordinate treatment of the ligand-free Co_3CCH_3 and $-CD_3$ core, and we find the conclusions of these authors entirely convincing on this point.

The bands at 991 and 742 cm^{-1} must then belong to the antisymmetric and symmetric C–S stretches, respectively. The higher one of these frequencies lies quite near to the highest end of the zone found to be characteristic for the predominance of the resonance structure shown by **1**,[55] some 35 cm^{-1} lower



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than the corresponding band of the xanthate complexes. However, the (squared) average of the symmetric and asymmetric ν(C–S) frequencies (875.5 cm^{-1}) is quite high in this case, owing to the smaller separation of them than the one found, e.g., in di- and trithiocarbonato complexes.[55] Hence a rough calculation yields 394 nm^{-1} for the C–S stretching force constant, to be compared with 370 nm^{-1} found for bis(ethyl xanthato)nickel(II) and 780 nm^{-1} obtained for pure CS_2.[55,56]

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(49) Some resemblance is shown by the $HRu_3(CO)_9C_6H_9$ complex,[50] in which the five-electron-donor allene-type ligand is σ and π bonded to the cluster and the central C atom coordinates to two Ru atoms.

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(53) For a critical survey of the features of bridging CO groups see R. Colton and M. J. McCormick, *Coord. Chem. Rev.*, **31**, 1 (1980).

(54) P. Skinner, M. W. Howard, I. A. Oxton, S. F. A. Kettle, D. B. Powell, and N. Sheppard, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1203 (1981).

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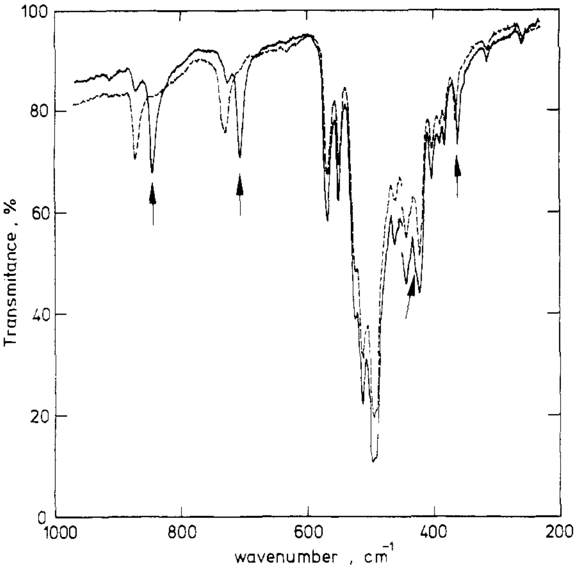

Figure 7. IR spectrum of $Co_6(CO)_{15}CS_3$ (Ib) in the 1000–200-cm^{-1} region (CsI pellet): dashed line, natural ^{12}C abundance; solid line, sample prepared from $^{13}CS_2$ (90% ^{13}C). Arrows indicate isotopically shifted bands.

(b) $[(CO)_8Co_3]CS_2[Co_3(CO)_7S]$ (Ib). ^{13}C-Substitution Study of the Vibrational Frequencies of the Pentacoordinate Carbon Atom. Owing to the fact that the CS_2 unit in this case is no longer a "free", dithiocarboxylato-type linking group but it is rather firmly built into a cluster, a simple treatment in terms of two C–S stretches and a Co–C one is not justified.

As shown by the comparison of the spectra of the "natural" and of the centrally ^{13}C-enriched (90%) samples (Figure 7), both bands present above the carbonyl region suffer quite substantial frequency shifts upon ^{13}C substitution. The one at 870 cm^{-1} is shifted by 28 cm^{-1} and the other one at 729 cm^{-1} by 25 cm^{-1} toward lower energy. Hence both vibrations must be prevalently located on the carbon atom.

The carbon atom of the cluster-bonded CS_2 unit has three degrees of vibrational freedom. Two of these vibrations should occur within the idealized mirror plane of the molecule, and one must be perpendicular to it. These three vibrational modes of the carbon atom can be derived from the symmetric (i.e., species a_1) and asymmetric (i.e., belonging to the doubly degenerate species e) Co–C vibrations of a Co_3C pyramid (point group C_{3v}) present in the enneacarbonyltricobalt carbon complexes.

In a previous ^{13}C-enrichment study we have found the symmetrical Co–C stretching mode of the $Co_6C(CO)_{12}S_2$ cluster at 819 cm^{-1} (^{12}C–^{13}C frequency shift 29 cm^{-1}), and the perpendicular (e′) mode could be assigned at 548 cm^{-1} (^{12}C–^{13}C shift 12.5 cm^{-1}).[27,57] By analogy we assign the highest band at 870 cm^{-1} to the in-plane (a′) vibration along the Co(3)–C(16) bond. The ^{12}C band at 729 cm^{-1} has a strikingly high frequency and should therefore reflect strong restoring forces. Therefore we suggest assignment of this band to the perpendicular (a″) mode, where the asymmetric C–S stretching character should dominate, reinforced by the corresponding components of the bridging Co–C bonds. The considerably reduced C–S bond order, as compared with the one in V, is then reflected by the much lower frequency found for Ib.

It is difficult to suggest the frequency of the third C atom mode, viz., the one of the a′ vibration perpendicular to the sp^2 plane. The lowest ^{12}C–^{13}C band pair at 375 and 371 cm^{-1} seems to be too low for such a mode: the ν_{as}(Co–C) has been assigned at 555 cm^{-1} for $CH_3CCo_3(CO)_9$ and at 536 cm^{-1} for the CD_3 analogue[54] although it must be emphasized that the agreement between calculated and observed values is just for these cases the poorest in the study of Skinner et al. For $HCCo_3(CO)_9$ and $DCCo_3(CO)_9$ this kind of vibration is assigned at much lower frequencies, viz., at 417 and 410 cm^{-1}, but again the agreement between observation and calculation is poor.[58]

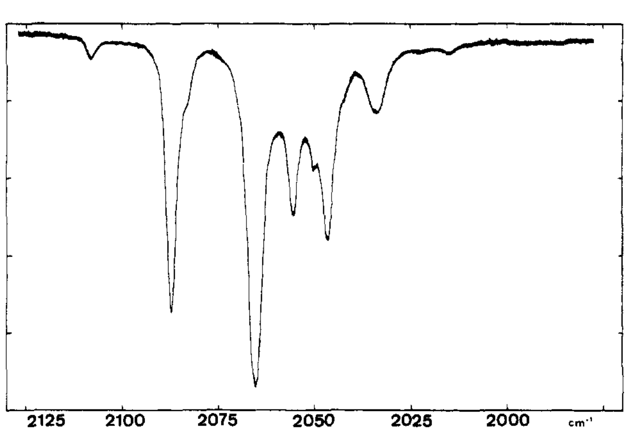

Figure 8. IR spectrum of $Co_6(CO)_{16}C_2S_3$ (V) in the C–O stretching region (solvent hexane, ca. saturated solution, 1-mm cell).

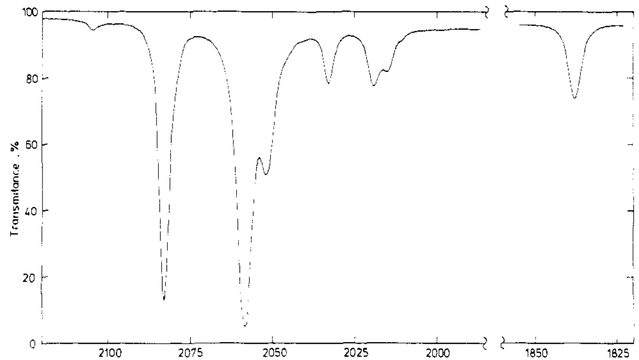

Figure 9. IR spectrum of $Co_6(CO)_{15}CS_3$ (Ib) in the C–O stretching region (solvent hexane, 0.5-mm cell).

Hence it is possible that in Ib this mode is hidden somewhere in the 430–450-cm^{-1} region, since the ^{13}C band (shoulder) at ca. 428 cm^{-1} has no ^{12}C counterpart. In this case the pair at 375 and 371 cm^{-1} would belong to a Co–CO stretching mode which is coupled with a displacement motion of the central carbon atom. The very low isotopic shift of 4 cm^{-1} seems to support this suggestion.

2. C–O Stretching Region. The pattern of the terminal region is quite similar for the two complexes, apart from the presence of a bridging ν(C–O) band for Ib at 1838 cm^{-1} (Figures 8 and 9). Although the point group C_s would allow all C–O stretching modes to be IR active, only half of the vibrations can be observed. There are eight ν(C–O) bands in the solution spectrum of V and seven of them in the terminal region of Ib. This phenomenon is quite general for the spectra of cluster carbonyls. So, e.g., only four bands are straightforwardly observed in the solution spectra of simple $YCCo_3(CO)_9$ compounds,[59] four to five instead of six for Co_4- and

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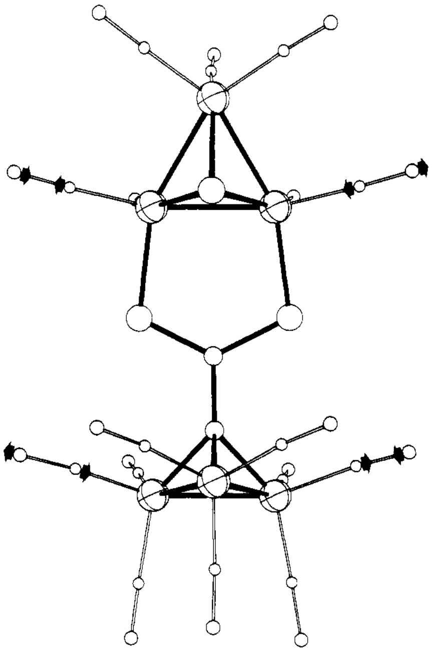

Figure 10. Schematic representation of a hypothetical C–O stretching normal vibration of species a″ in which the local oscillating dipoles cancel each other's intensity contribution.

$Rh_4(CO)_{12}$,[60] two instead of three for $Co_6C(CO)_{12}S_2$,[27] etc., and only ^{13}CO-enrichment studies and force constant calculations identified the position of the IR-active bands not directly observed.

Also in the case of the closely related $[Co_3(CO)_7S]_2S_2$, only 7 bands were observed for 14 IR-active ν(C–O) modes and this led, in an early study, to the trinuclear formulation of $Co_3(CO)_7S_2$ for this compound.[61,62]

Whereas in the case of the above-mentioned closed "monoclusters" of high molecular symmetry an intensity cancellation by an induced metal–metal dipole was shown to be responsible for the apparent absence of one or two of the IR-active C–O fundamentals,[63] in the present cases we believe that another effect is operating. In point group C_s there are, at the most, pairs of equivalent internal C–O coordinates that can combine to give symmetry coordinates. The symmetry coordinates, in turn, can and must combine in many sign combinations to form the normal coordinates. Thus, about half of the normal coordinates have a form in which the relative phase (sign) of the symmetry coordinates (CO pairs or single CO groups, if they lie in the mirror plane) is such as to completely or nearly annihilate the overall dipole moment variation associated with that normal vibration. A simplified example for such a case is shown in Figure 10. In this combination of only two symmetry coordinates no overall dipole moment arises if the amplitudes and the relevant direction cosines are equal.

For the compounds under study, and for the related $[Co_3(CO)_7S]_2S_2$, there are three specific combinations of the symmetry coordinates which give rise to characteristic frequencies and/or intensities, and these belong to the three bands of highest energy. The highest C–O stretching frequencies in the 2100–2120-cm^{-1} region have been known for a long time[64] to belong to the totally symmetric in-phase ν(C–O) vibrations. In the present cases (2108 cm^{-1} for V, 2104.5 cm^{-1} for Ib; for comparison 2099.5 cm^{-1} for $[(CO)_7Co_3S]_2S_2$[61]) the intensity of this band is very low, as compared to that of the $YCCo_3(CO)_9$ compounds, since the in-phase coupling of the local vibrations of the two $Co_3(CO)_x$ subunits causes a strong overall compensation of the local intensities.

The second band is quite strong (at 2087 cm^{-1} for V and at 2083 cm^{-1} for Ib), and it belongs with certainty to the vibration when all the ligands on one Co_3 unit vibrate locally in phase but the two $Co_3(CO)_x$ entities couple out of phase. The separation between the highest band and the present one is a cumulative measure of the Co···C′O′ couplings between the two $Co_3(CO)_x$ subunits. For simple $Co_3(CO)_xE$ complexes no bands occur in this region. For $[(CO)_7Co_3S]_2S_2$, this band occurs at 2074 cm^{-1}. The high intensity of this band includes with certainty also an induced dipole contribution along a longitudinal molecular axis, since one Co_3 unit obtains a δ^+ and at the same time in the other Co_3 entity a δ^- partial charge in the same phase of the vibration.

The third band (at 2065.5 cm^{-1} for V and at 2058.5 cm^{-1} for Ib) is the strongest of the whole spectrum, similar to that for $[SCo_3(CO)_7]_2S_2$, where the analogous frequency occurs at 2049.5 cm^{-1}. This type of vibration can be derived for the very strong e mode of the monopyramidal $Co_3(CO)_9E$ (E = CY or S) complexes. The corresponding frequencies were observed, e.g., at 2065 cm^{-1} for $CH_3O(CO)CCo_3(CO)_9$,[59a] at 2057 cm^{-1} for $HCCo_3(CO)_9$[59a,d] and at 2049.5 cm^{-1} for $Co_3(CO)_9S$.[8,61] In the case of the dipyramidal hexacobalt clusters this is an a″ species vibration, in which all C–O groups on one side of the plane of symmetry vibrate in phase and those on the other side in the opposite phase. (The ligands lying within the mirror plane do not vibrate.) The high intensity is the result of the vectorial summation, with the same sign, of all out-of-plane oscillating C–O dipoles.

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Registry No. Ib, 82112-99-0; V, 74304-57-7.

Supplementary Material Available: Listings of observed and calculated structure factors, thermal anisotropic parameters, bond distances and angles, and equations of the weighted planes, deviations from them, and dihedral angles for complexes V and Ib (39 pages). Ordering information is given on any current masthead page.

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